The Value of the Rydberg Constant for Spectral Series.

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Introductory.

In a previous paper,* the results of a series of measurements of the wave-lengths of the first six lines of the Balmer series of hydrogen were given, together with a determination of the Rydberg constant for spectral series. It has recently been pointed out to me by Prof. Fowler that the value of the series constant there obtained is not quite correct, in consequence of errors in the corrections applied to the observed wave-lengths to reduce them to *vacuo,* the data employed for this purpose having been taken from a Table† appropriate to wave-lengths in air at 20° C., whereas the tertiary standards of iron upon which the wave-length determinations were based referred to 15° C. Before the introduction of the International system, wave-lengths had always been given for air at 20° C., and there was no explicit mention of the change of standard temperature in the paper‡ by Burns, from which the iron arc wave-lengths used as standards were taken. The oversight might possibly have been detected earlier but for the author's absence on military service from September, 1914, to January, 1919. In any case, however, a revision of the previous work would have been necessary in view of the recent accurate determinations at the Bureau of Standards of the refractive index of air,§ and also of other work, both theoretical and experimental, on the Balmer series, which has been carried out since 1914.

The correction in question is of the order of $+0{\cdot}02$ A., and results, as will be seen, in a decrease of nearly one unit in the value of the Rydberg constant.

Corrected Wave-lengths and Wave-numbers.

The corrected values of the wave-lengths (*in vacuo*) and wave-numbers are tabulated below. The last column gives the values of N derived from each line by applying the Balmer formula. Although the observed wave-lengths in air are only recorded to the third place of decimals, it is advisable to take

* 'Roy. Soc. Proc.,' A, vol. 90, p. 605 (1914).

† Kayser, 'Spectroscopie,' vol. 2, p. 514.

‡ 'Lick Obs. Bull,' vol. 8, No. 247 (1913).

§ Bureau of Standards, Washington, 'Scientific Papers,' No. 327 (1918).

out the corrections to the fourth place, in order to prevent the possibility of accumulated error affecting the third figure.

Table I.

m.	λ air.	Correction.	λ vac.	ν vac.	$\frac{4m^2\nu}{m^2-4}$.
3	6562·793 I.A.	+1·8092	6564·6022	15233·216	109679·155
4	4861·326	+1·3537	4862·6797	20564·793	109678·896
5	4340·467	+1·2160	4341·6830	23032·543	109678·776
6	4101·738	+1·1535	4102·8915	24373·055	109678·748
7	3970·075	+1·1190	3971·1940	25181·343	109678·738
8	3889·051	+1·0979	3890·1489	25705·957	109678·750

The systematic variation of N, of magnitude exceeding that which could be attributed to experimental error, indicates, as was previously found to be the case, that the Balmer formula is only an approximation to the truth.

Discussion of Formulæ Investigated.

The formulæ examined may all be written in the form

$$\nu = \mathrm{N}\left(\frac{1}{4}-\frac{1}{m^2}\right)+f(m, \mathrm{N}).$$

Since Balmer's law is so nearly exact, $f(m, \mathrm{N})$ is of the nature of a small correction to $\mathrm{N}\left(\frac{1}{4}-\frac{1}{m^2}\right)$, never exceeding 0·002 per cent. of the latter quantity in any of the formulæ under discussion. The exact form of this function, however, exercises an important influence on the value obtained for N.

It is natural to try first a formula of the Rydberg type, viz.:—

$$\nu = \frac{\mathrm{N}}{(2+p)^2}-\frac{\mathrm{N}}{(m+\mu)^2}. \tag{I}$$

The most convenient method of solution is to assume an approximate value, N′, such that the true value $\mathrm{N} = \mathrm{N}'+\delta\mathrm{N}$. Then, neglecting the second and higher powers of p and μ, we obtain

$$\delta\mathrm{N}+\frac{8\mu\mathrm{N}'}{m(m^2-4)}-\frac{\mathrm{N}'pm^2}{m^2-4} = \frac{4m^2\nu}{m^2-4}-\mathrm{N}'.$$

A least-squares solution gives

$$\mathrm{N} = 109678{\cdot}278, \qquad \mu = +0{\cdot}0_5210, \qquad p = -0{\cdot}0_5383.$$

This, as will be seen from Table II, represents the results satisfactorily, but, before adopting this formula, it is necessary to examine whether an equally good representation of the series can be obtained by employing only two constants.

Retaining μ and N, the formula becomes

$$\nu = \frac{N}{4} - \frac{N}{(m+\mu)^2}. \tag{II}$$

The least-square values are

$$N = 109678{\cdot}725, \qquad \mu = +0{\cdot}0_5 74.$$

The observed *minus* calculated values suggest a slight inferiority to formula (I), but not more than would be expected in view of the elimination of one constant. Since the representation is within the limits of probable experimental error, one must conclude that the introduction of the third constant is not justifiable.

Retaining p instead of μ, the formula becomes

$$\nu = \frac{N}{(2+p)^2} - \frac{N}{m^2}. \tag{III}$$

A least-square solution gives

$$N = 109678{\cdot}10, \qquad p = -0{\cdot}0_5 53.$$

This again appears to be quite satisfactory as regards the numerical agreement with the observed wave-lengths. The superiority over (II), however, is too slight to warrant the definite adoption of (III) in preference to (II), but the conclusion is confirmed that the present data do not necessitate a formula including more than two constants.

Turning now to theoretical investigations in connection with the radiation of the hydrogen atom, Dr. Bohr has modified his well-known derivation of the Balmer formula by introducing a small correction due to the dependence of the mass of the electron upon its velocity.* He thus obtains the formula

$$\nu = N\left(\frac{1}{4} - \frac{1}{m^2}\right)\left\{1 + k\left(\frac{1}{4} + \frac{1}{m^2}\right)\right\} \tag{IV}$$

Applying this to the observed wave-numbers, the method of least-squares gives

$$N = 109677{\cdot}58, \qquad k = +0{\cdot}0_4 387.$$

It will be seen from Table II that this formula is inferior to either (II) or (III), both of which employ the same number of constants, namely, two. The 0 *minus* C residuals exceed the probable error of the wave-length determination in two cases, viz., $H\gamma$ and $H\zeta$, the former being the best determined line of the six. Moreover, the deviation tends to be systematic, a feature which is brought out very distinctly by calculating the constants from two lines instead of by the method of least-squares.

* 'Phil. Mag.,' vol. 29, p. 332 (1915).

The theoretical expression for k is $\pi^2 e^4/c^2 h^2$, where

$$e = \text{charge of electron,}$$
$$c = \text{velocity of light,}$$
$$h = \text{Planck's element of action.}$$

This, when evaluated, gives $k = +0{\cdot}0_4 133$, about one-third of the value found above. The sign and order of magnitude are certainly right, and the discrepancy is possibly no more than could be attributed to error arising from the compound nature of the lines, a point which is considered in the succeeding section.

Dr. Allen, by taking account of the magnetic moment of the atomic nucleus, has obtained an expression of the form

$$\nu = \frac{N}{4} - \frac{N}{\left(m + \frac{B}{m^2}\right)^2}. \tag{V}$$

The least-square values derived from this formula are

$$N = 109678{\cdot}76, \qquad B = +0{\cdot}0_4 629.$$

It is singular that the value of B should agree precisely with that obtained by Allen on the assumption of five magnetons, but the exactness of the agreement can only be accidental. Moreover, the residual for Hβ is distinctly too large to permit us to regard this type of formula as satisfactory. In fact, neither this nor formula (IV) seems to be of a quite suitable shape to represent the observed values. It is considered that these latter are hardly likely to be in error by more than the amounts shown in the third column of Table II, in view of the fact that the Rydberg type of formula gives such good results.

The formula originally proposed by Dr. Allen was more general than the above, and was of the form

$$\nu = \frac{N}{\left(2 + \frac{B}{4}\right)^2} - \frac{N}{\left(m + \frac{B}{m^2}\right)^2}. \tag{VI}$$

With this type of formula, B is necessarily negative, but there would seem to be no objection to this on theoretical grounds. A least-square solution gives

$$N = 109677{\cdot}79, \qquad B = -0{\cdot}0_4 3144.$$

The representation is much better than in the case of V, the residuals being comparatively small, but they exhibit a distinct tendency towards systematic variation, so that the formula cannot be considered so good as any of the Rydberg forms. It may be noted, however, that the above value of B is

exactly that obtained theoretically on the assumption of three magnetons in the core of the atom.

One other type of formula has been examined, and the results are perhaps worth recording, although it does not give a quite satisfactory fit, nor has it any theoretical basis so far as is known. The only point of interest in connection with it is that only one constant is employed. If we write 1/N for μ in formula (II) we get

$$\nu = \frac{N}{4} - \frac{N}{\left(m+\frac{1}{N}\right)^2}. \tag{VII}$$

The average value of N is 109678·70, and the only sensible residual is that corresponding to Hα, which, however, is too large to be admissible.

Table II.—Comparison of Formulæ.

m.	λ obs. (air).	Probable error $\times 10^4$.	(λ obs. $-$ λ calc.) $\times 10^4$.						
			(I.)	(II.)	(III.)	(IV.)	(V.)	(VI.)	(VII.)
3	6562·793 I.A.	±17	+2	+2	−2	−11	+6	−6	−47
4	4861·326	10	−9	−16	−6	+5	−30	+5	+9
5	4340·467	6	+8	+4	+8	+15	0	+13	0
6	4101·738	13	+5	+3	+3	+5	+7	+5	−3
7	3970·075	16	−1	+1	−2	−4	+7	−4	+5
8	3889·051	11	−7	−4	−9	−15	+3	−13	+11
		$\Sigma\Delta$	−2	−10	−8	−5	−7	0	−25
		$\Sigma\Delta^2$	224	302	198	637	1043	440	2445

Effect of Composite Structure of Lines.

Before attempting to decide upon the best value to adopt for N, in view of the foregoing discussion of formulæ, it is necessary to take account of the structure of the lines. It has long been known that at least two components existed in the case of Hα and Hβ, and presumably this complexity exists also in the other members. Obviously, then, for the complete representation of the series as many formulæ as there are components will be required, and the value of N derived from measurements of the unresolved lines (as they were in the present case) will not necessarily be the true one. If the intensity distribution were very unsymmetrical an appreciable error might be introduced in this way. An attempt has been made to estimate the amount of the uncertainty due to this cause, but it is difficult to do so with any degree of exactitude. In the first place, the precise structure would still appear to be in some doubt. Bohr mentions "the fact that the hydrogen

lines, when observed by instruments of high dispersive power, are split up in a number of components situated close to each other," but the reference is not given, and has not yet been traced.

According to the observations of Merton and Nicholson,* $H\alpha$ and $H\beta$ are doublets, the separations (0·132 and 0·030 respectively) corresponding to a principal type of series. They agree with previous investigators that the ratio of intensities is about 10 : 7, the less refrangible component being the stronger. If it be assumed that the wave-length determinations really refer to the " optical centre of gravity," *i.e.*, a point 7/17 of the separation from the less refrangible component, and if it be further supposed that the series is of the principal type, it is possible to calculate the wave-lengths of the individual components. The former assumption would hardly be permissible if their actual wave-lengths were required, but the object here is merely to estimate to what extent the duplicity of the lines may affect the value of N.

If we adopt formulæ of type II we shall have

$$\nu' = \frac{N}{4} - \frac{N}{(m+\mu')^2}, \qquad \nu'' = \frac{N}{4} - \frac{N}{(m+\mu'')^2}$$

The wave-number interval,

$$d\nu = \nu' - \nu'' = \frac{N}{(m+\mu'')^2} - \frac{N}{(m+\mu')^2} = \frac{2(\mu'-\mu'')N}{m^3}, \text{ approx.,}$$

and the wave-length interval

$$d\lambda = -\frac{\lambda}{\nu}d\nu = \frac{2\lambda(\mu''-\mu')N}{\nu m^3} = \frac{32\times 10^8(\mu''-\mu')}{N} \times \frac{m}{(m^2-4)^2},$$

or $d\lambda = \dfrac{km}{(m^2-4)^2}$, where k is a constant which can best be determined from the separation of $H\alpha$.

Assuming for this the value 0·132, the separations of $H\beta$, etc., come out 0·031, 0·012, 0·007, 0·004, and 0·002 respectively.

Table III.

Less refrangible components.		More refrangible components.	
Assumed λ (air).	O−C.	Assumed λ (air).	O−C.
6562·847 I.A.	+0·000	6562·715 I.A.	+0·000
4861·339	−0·001	4861·308	−0·001
4340·472	+0·001	4340·460	+0·001
4101·741	+0·000	4101·734	+0·001
3970·077	+0·000	3970·073	+0·000
3889·052	−0·000	3889·050	−0·000

* 'Phil. Trans.,' A, vol. 217, p. 237 (1917).

By applying the first assumption the wave-lengths given in Table III were obtained. The calculation of formulæ of type (II) for these gave $N = 109678{\cdot}73$, $\mu' = -0{\cdot}0_5 82$, $\mu'' = +0{\cdot}0_4 30$.

As will be seen, the fit is satisfactory in both cases, and there is no appreciable change in the value of N. If instead of formula (II), either (I) or (III) be used, a similar result follows, that is to say, the values of N respectively obtained differ but little from those already given. So that if the doublets are really of principal type, or, more generally, if they show a rapid decrease of wave-number interval as m increases, the consequent uncertainty in the value of N is not serious.

If instead of dealing with the "optical centre of gravity" it be supposed that the settings were made midway between the edges of the lines (and this is certainly what was attempted), the values of μ become $-0{\cdot}0_4 12$ and $+0{\cdot}0_4 27$, and again there is no appreciable change in the value of N.

On the other hand, the values obtained for μ are considerably affected by the question of the structure of the lines, and cannot be determined with any degree of accuracy from measurements on unresolved doublets. Two interesting possibilities present themselves, however, and may be noticed here. One is that the Balmer law may hold rigorously for one of the components of each line. The fact that the μ of formula (II) comes out positive excludes this possibility as far as the more refrangible component is concerned, and a simple calculation shows that for the less refrangible component, μ could only be zero if the settings had been made on a point situated about one-fifth of the separation (0·132) from the latter component. This would appear to require a much larger difference of intensity than has been found experimentally, so that in all probability neither component is exactly represented by the Balmer formula.

The second possibility in question is that the components of each line may be symmetrically situated on either side of the positions indicated by Balmer's law. If this were so, μ' and μ'' would be equal and of opposite signs, and it is found that the measurements would have to be taken as referring to a point five-sevenths of the separation from the less refrangible component. This would only be the case if the more refrangible were the stronger, which is again in disagreement with the experimental evidence.

The Value of the Series Constant.

From the preceding remarks, it will be seen that the chief difficulty in determining the most probable value of N arises not so much from the non-homogeneity of the lines as from the uncertainty as to the proper type of

formula to be adopted. The results given by the various formulæ are summarised below:—

$$\text{(I.)}\qquad \nu = \frac{\mathrm{N}}{(2+p)^2} - \frac{\mathrm{N}}{(m+\mu)^2}, \qquad \mathrm{N} = 109678{\cdot}28.$$

$$\text{(II.)}\qquad \nu = \frac{\mathrm{N}}{4} - \frac{\mathrm{N}}{(m+\mu)^2}, \qquad \mathrm{N} = 109678{\cdot}73.$$

$$\text{(III.)}\qquad \nu = \frac{\mathrm{N}}{(2+p)^2} - \frac{\mathrm{N}}{m^2}, \qquad \mathrm{N} = 109678{\cdot}10.$$

$$\text{(IV.)}\qquad \nu = \mathrm{N}\left(\frac{1}{4} - \frac{1}{m^2}\right)\left\{1 + k\left(\frac{1}{4} + \frac{1}{m^2}\right)\right\}, \qquad \mathrm{N} = 109677{\cdot}58.$$

$$\text{(V.)}\qquad \nu = \frac{\mathrm{N}}{4} - \frac{\mathrm{N}}{\left(m + \frac{\mathrm{B}}{m^2}\right)^2}, \qquad \mathrm{N} = 109678{\cdot}76.$$

$$\text{(VI.)}\qquad \nu = \frac{\mathrm{N}}{\left(2 + \frac{\mathrm{B}}{4}\right)^2} - \frac{\mathrm{N}}{\left(m + \frac{\mathrm{B}}{m^2}\right)^2}, \qquad \mathrm{N} = 109677{\cdot}79.$$

It will be observed that the two theoretical formulæ (IV) and (VI) give the lowest values, but neither can be regarded as definitely supported by the experimental results. From the latter point of view, (I), (II), and (III) are all satisfactory and about equally good. For the present, until accurate determinations of the wave-lengths of the components (particularly of $\mathrm{H}\alpha$) become available, the adoption of 109678·3 as a provisional value is suggested. This is in agreement with that derived from (I), and is roughly intermediate between (II) and (III).

The amount of the uncertainty, about 0·5 at most, is probably not of serious consequence, having regard to the degree of accuracy of our present data in the case of most of the series lines of other elements. The same is true with reference to the correction (−0·9) now applied to the value (109679·2) given in the previous paper. Thus, for example, the conclusion of Nicholson,* that the Rydberg constant derived from the Balmer series is also applicable to the helium series, does not require modification on this account.

The wave-lengths of all the lines down to $m = 37$ have been recalculated in the hope that they may possibly prove of service in certain cases, such as, for example, the reduction of eclipse spectra, particularly those obtained with slitless spectrographs. Formula (I) was used for the purpose, and the differences from the previous values are extremely small, never more than 0·001 A, in fact. The new values are given in Table IV below:—

* 'Roy. Soc. Proc.,' A, vol. 91, p. 255 (1915).

Table IV.—Wave-lengths (in Air) of Balmer Series Lines calculated by Formula (I).

m.	λ (I.A.).	*m.*	λ (I.A.).	*m.*	λ (I.A.).
3	6562·793	15	3711·973	27	3666·097
4	4861·327	16	3703·855	28	3664·679
5	4340·466	17	3697·154	29	3663·405
6	4101·738	18	3691·557	30	3662·258
7	3970·075	19	3686 834	31	3661·221
8	3889·052	20	3682·810	32	3660·280
9	3835·387	21	3679·355	33	3659·423
10	3797·900	22	3676·365	34	3658·641
11	3770·633	23	3673·761	35	3657·926
12	3750·154	24	3671·478	36	3657·269
13	3734·371	25	3669·466	37	3656·666
14	3721·941	26	3667·684	∞	3645·981

The above formula gives the convergence wave-number *in vacuo* as 27419·674, corresponding to a wave-length in air of 3645·981 I.A., which is exactly the same as that obtained in the previous paper.

Summary.

(1) The results given in a previous paper have been modified on account of a slight alteration now found to be necessary in the values of the corrections to vacuum.

(2) A number of formulæ, empirical and theoretical, have been compared, and it is found that a two-constant Rydberg formula is capable of representing the series satisfactorily, and shows an appreciable superiority in this respect over the theoretical formulæ of both Bohr and Allen.

(3) The probable effect upon the determination of N arising from the composite structure of the lines is investigated, and found to be inappreciable, except in so far as this non-homogeneity renders it somewhat uncertain which type of formula should be employed to represent the observed wave-lengths.

(4) The provisional adoption of the value 109678·3 for N is suggested. This is probably sufficiently accurate for present purposes, but could be improved upon if accurate wave-lengths of the individual components of $H\alpha$ and $H\beta$ were available.

(5) The calculated wave-lengths of the members of the series down to $m = 37$ are given. These do not differ by more than 0·001 A from the corresponding values given previously.